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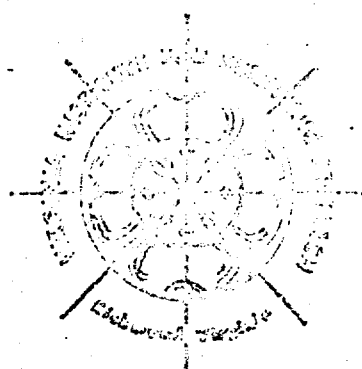
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THE ACCELERATED CORROSION OF METALS

David A. Jackson, Jr.

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Contractor: Army Chemical Center  
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Seventh Quarterly Report

Covering the Period

March 16 - June 15, 1961

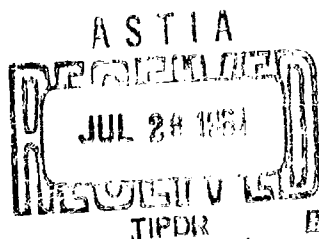
Title: THE ACCELERATED CORROSION OF METALS

Prepared By

Senior Investigator: Henry Leidheiser, Jr.  
Associate: David A. Jackson, Jr., Research Chemist

July 14, 1961

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## INTRODUCTION

In previous reports (1), the oxidation of aluminum in contact with mercuric halides has been studied, and the factors which influence the oxidation rates have been determined. In this report period the Al-HgI<sub>2</sub> system has been used for quantitative measurements of the oxidation rates.

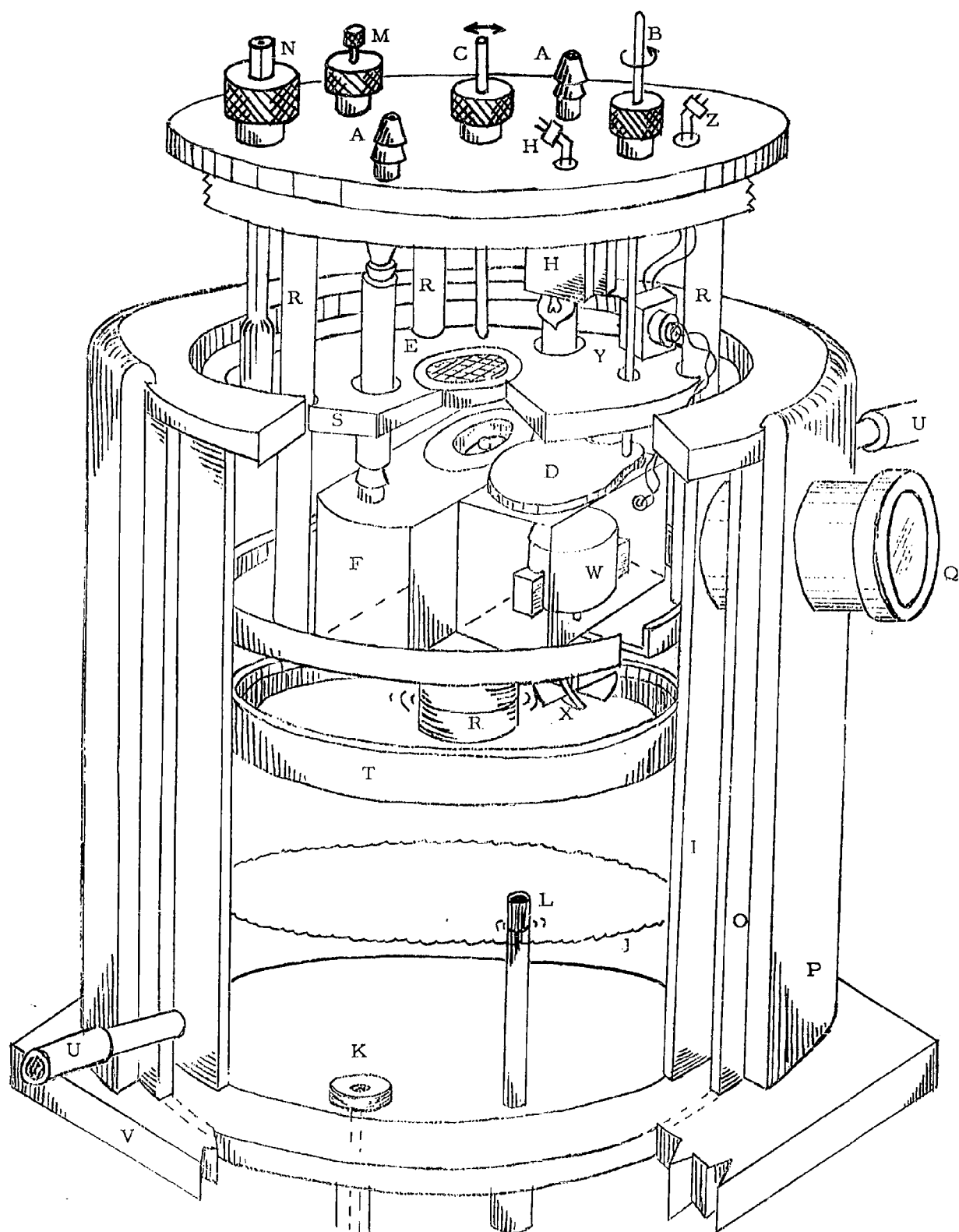
In the Sixth Quarterly Report the necessity for close temperature control of the sample was determined. In the present report, the importance of the relative humidity has been investigated. The rate of oxidation of aluminum in air in the presence of HgI<sub>2</sub> has been studied over a relative humidity range of 40-100%.

## DESCRIPTION OF APPARATUS

The apparatus described in the Sixth Quarterly Report has been modified to include a small fan to stir the internal atmosphere of the chamber, and a plastic tray to hold different saturated salt solutions by which constant relative humidities were obtained. A diagram of this modified reaction chamber is seen in Figure 1. At relative humidities less than 100% Octoil-S having a very low vapor pressure was used as the variable spacer instead of water. At 100% relative humidity no salt solutions were used, and water was used as the variable spacer as well as for the source of water vapor.

Figure 1 - Reaction Chamber

3.



- A - Water Connections to Sample Jacket
- B - Sealed Shield Rod
- C - Sealed Agitator Rod
- D - Shield
- E - Nylon Gauze sieve
- F - Sample Water Jacket
- G - Sample Cup
- H - Bulb, Housing and Sealed Connection
- I - Inner Jacket
- J - Water Level or Octoil-S Level (Variable Spacer)
- K - Capillary Water Manometer
- L - Capillary Mercury Manometer
- M - Equilizing Bleeder
- N - Sealed Thermometer
- O - Outer Jacket
- P - Asbestos Insulation
- Q - Sealed Observation Window
- R - Plastic Posts
- S - Plastic Tables
- T - Plastic Tray for Saturated Salt Solutions
- U - Water Connections to Outer Jacket
- V - Base
- W - Plastic Encased 3 v. Fan Motor
- X - Fan
- Y - Motor Jack and Housing
- Z - Sealed Motor Connection

## EXPERIMENTAL PROCEDURE

Reynolds 99.999% aluminum cylinders 1/2" in diameter and 1/4" thick, were given the routine pretreatment for sample preparations as stated in previous reports. Exposed surface areas measured approximately 1.25 cm<sup>2</sup>.

The desired relative humidity was obtained by placing a saturated salt solution in the plastic tray (T) and allowing the enclosed system to reach equilibrium during a 1-2 hour period. Both thermal and humidity equilibrium were facilitated by the use of a small fan (X) which continually stirred the internal atmosphere. Upon reaching equilibrium, the reaction was begun as described in previous reports. Measurements of time, temperature and pressure were made at 5 to 10 minute intervals until the oxidation slowed or completely stopped. Corrections due to changes in barometric pressures were made when necessary.

The first values of  $\Delta P$ , when in cm H<sub>2</sub>O or cm Octoil-S, were converted to mm Hg. Later values of  $\Delta P$  were read directly from the mercury manometer. The values of  $\Delta P$  in mm Hg were then converted to  $\Delta W_{O_2}$  in mg/cm<sup>2</sup>. The equation for conversion of  $\Delta P$  to  $\Delta W$  (Sixth Quarterly Report, page 7) was found invalid under the existing conditions. The necessity for a moving atmosphere, as well as other considerations, made previous measurements of the oxidation rates inaccurate and unreliable. Values of  $\Delta W_{O_2}$  (mg/cm<sup>2</sup>) in this report were obtained by the conversion of  $\Delta P$  mm Hg from the following:

$$\Delta W = \frac{VM}{1.25R} \cdot \frac{\Delta P}{T}$$

where  $\frac{VM}{1.25R}$  was constant throughout the experiments.

Values of  $\Delta W$  were plotted vs. time for each experiment; the slopes of the linear portions of the curves were determined.

Several saturated salt solutions and the associated relative humidities which were obtained from these solutions are listed in Table A.

TABLE A

Relative Humidities of Several Saturated Salt Solutions at 30°C

<u>Solution</u>	<u>R. H. (%)</u>
Distilled Water	100
$BaCl_2 \cdot 2H_2O$	85
$(NH_4)_2SO_4$	81.1
$NH_4Cl + KNO_3$	68.6
$NaBr \cdot 2H_2O$	55
$Zn(NO_3)_2 \cdot 6H_2O$	40

## RESULTS AND DISCUSSION

As in previous determinations, the rate curves obtained during the oxidation of aluminum in contact with mercuric iodide were linear during a significant time interval. Whereas in these earlier experiments the linear portion of the curves were sometime preceded by low-rate induction periods, in the present experiments no great induction period seemed to exist. Usually within the first ten minutes the oxidation proceeded to an extent great enough to be measured on the manometer.

The slopes of the linear portions of the rate curves were approximately the same at any particular relative humidity. However, as the relative humidity decreased, the slopes of the rate curves also decreased. The slopes of the rate curves are listed in Table B, with the existing relative humidities obtained from the saturated salt solutions.

At low relative humidities (55% and below) the extent of oxidation was very small and the associated slopes for the rate curves could only be determined from the first few measurements in the 125-minute time interval. Reproducible results were difficult to obtain at low relative humidities; the oxidation slowed down soon after the initial attack by the mercuric iodide.

Figures 2 through 5 are experiments at 100% R.H.; Figures 6 through 9 at 85% R.H.; Figures 10 through 13 at 81.1% R.H.; Figures 14 through 16 at 68.6% R.H.; and Figure 17 at 55% and 40% R.H. Since the scales on all graphs are identical, comparison of Figure 16 with Figure 17 clearly indicates the sudden change in the final extent of oxidation between 68.6% R.H. and 55% R.H.

TABLE B

Values for the slopes of oxidation rate curves at different relative humidities  
at 30°C

Saturated Salt Solution Used	Relative Humidity (%)	Slope mgO <sub>2</sub> /cm <sup>2</sup> /min.	Ave. Slope mgO <sub>2</sub> /cm <sup>2</sup> /min.
Distilled Water	100	0.640	0.618
"	"	0.675	
"	"	0.526	
"	"	0.630	
BaCl <sub>2</sub> ·2H <sub>2</sub> O	85	0.613	0.559
"	"	0.556	
"	"	0.565	
"	"	0.500	
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	81.1	0.540	0.510
"	"	0.431	
"	"	0.515	
"	"	0.555	
NH <sub>4</sub> Cl + KNO <sub>3</sub>	68.6	0.447	0.446
"	"	0.430	
"	"	0.462	
NaBr·2H <sub>2</sub> O	55	0.193	0.206
"	"	0.218	
Zn(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	40	0.200	0.123
"	"	0.045	
Anhydrous CaSO <sub>4</sub> (Drierite)	0	no reaction	no reaction

An interesting observation was made concerning the appearance of the oxide at various relative humidities. At high relative humidities, the oxide was voluminous; sometimes growing from the samples in one continuous thick blue-white column. At low relative humidities, the oxide consisted of short fibers, somewhat powdery and pure white in color. It is thought that the degree and nature of hydration may account for the different in appearance. (2, 3, 4)

A 16 mm time-lapse movie was made of an aluminum sample being oxidized at 100% relative humidity at room temperature. The Cine-Kodak Special II camera was set to take one frame per second for a period of seventy minutes. Total viewing time for the seventy minute period was approximately 4.5 minutes. Excellent results were obtained under these conditions; the oxide growth was smooth and continuous.

Within three minutes after the initial attack by  $\text{HgI}_2$  and the subsequent amalgamation, the bulky fibers of aluminum oxide began to form at the edges of the sample. Oxidation from the center of the sample was somewhat later, with smaller filaments of oxide. On the movie film, the overall appearance was that of a flowering oxide growth as the fibers attained a length of several inches.

In Figure 18 average values of the different slopes are plotted vs. the relative humidities at which the slopes were determined. The change in slopes with change in relative humidity appears to be linear through the origin. Average values for the slopes at 55% and 40% are not included in this curve since the extent of oxidation, and number of experiments at these humidities

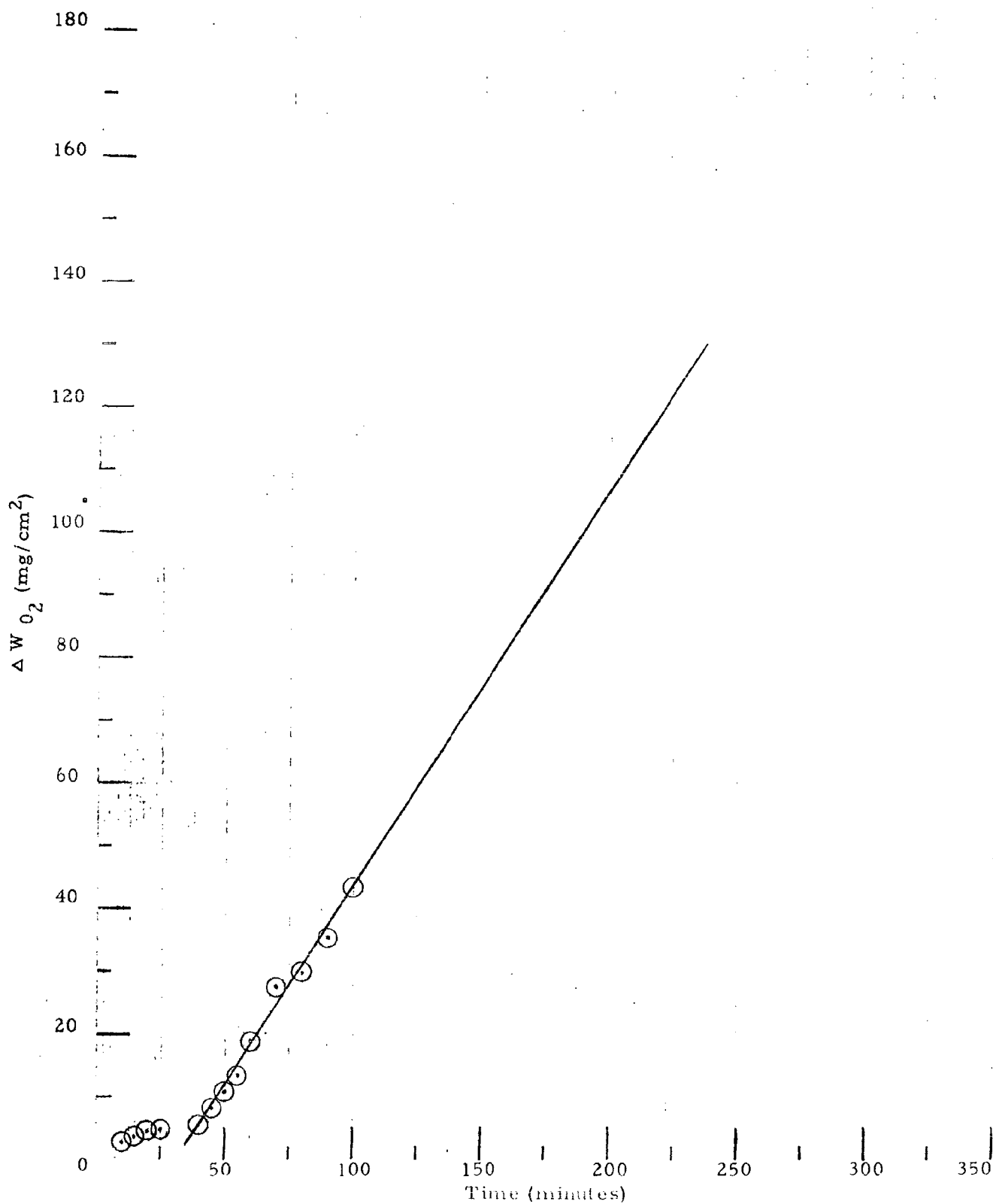
were not great enough to obtain significant results, and the reproducibility was poor. The value for the decrease of slope with decrease in relative humidity was  $0.633 \text{ mgO}_2/\text{cm}^2/\text{min}/\% \text{ R.H.}$  within the 68.6% to 100% relative humidity range. Below 68.6% R.H., the reactions became erratic; never oxidizing to any great extent.

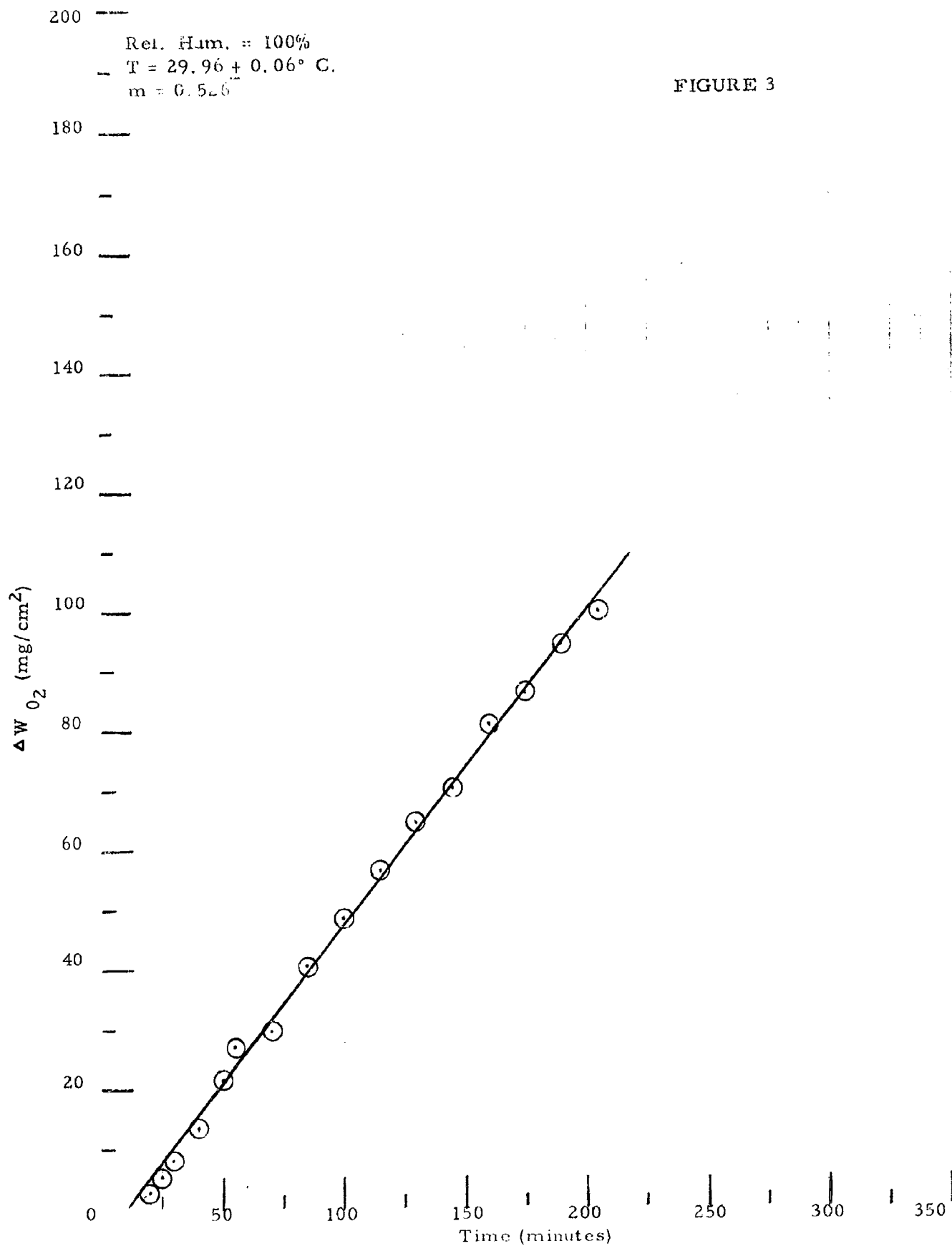
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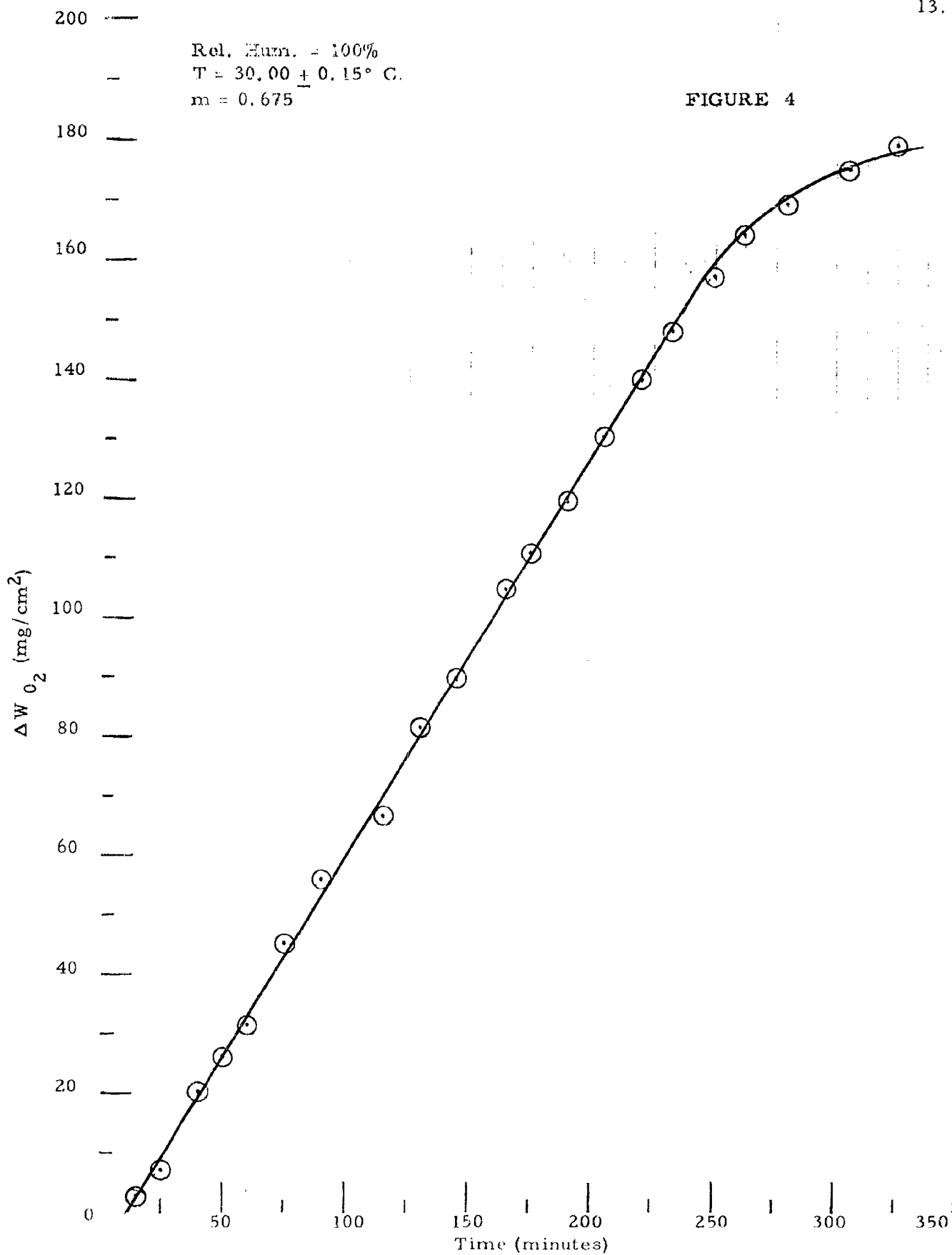
Rel. Hum. = 100%

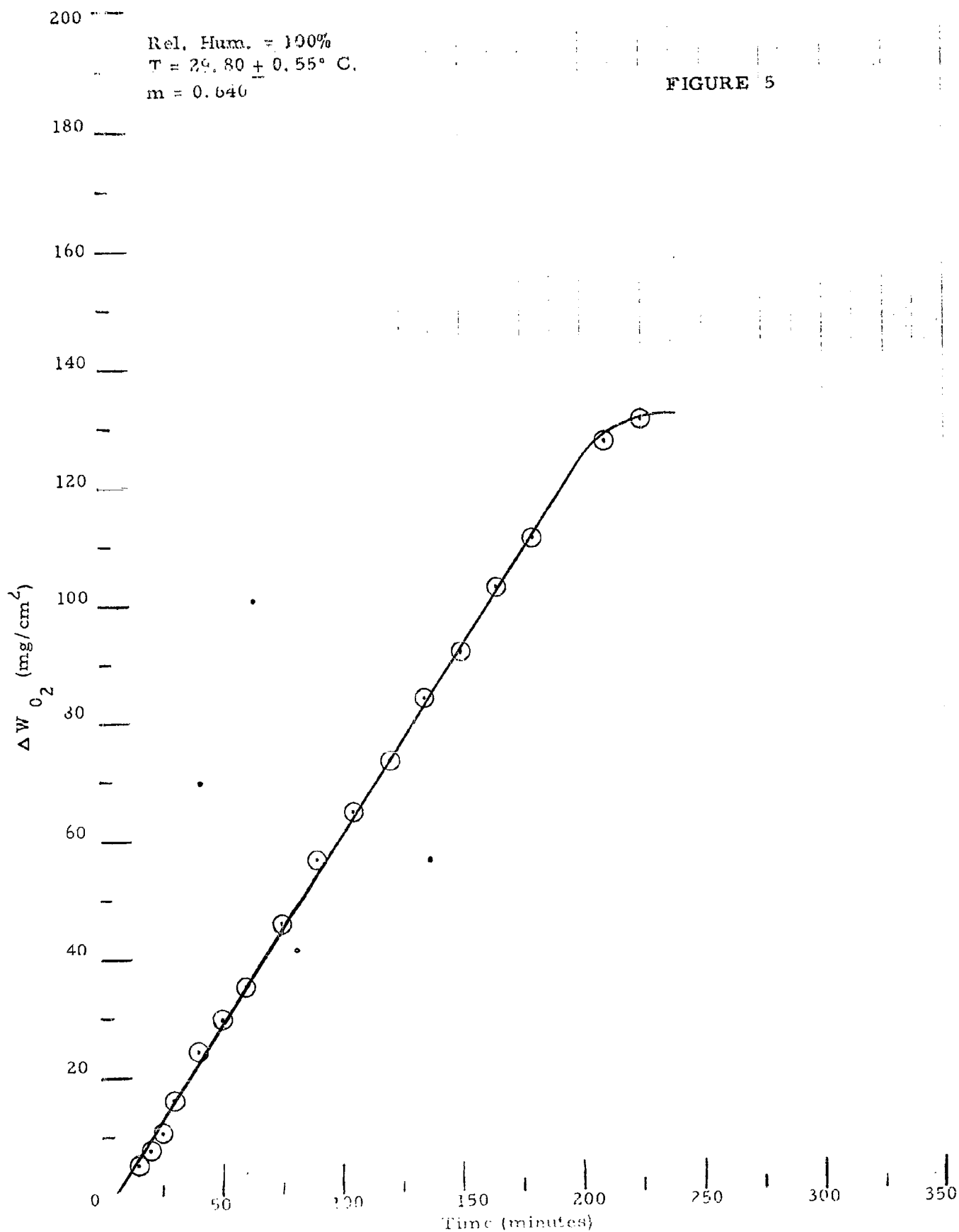
 $T = 30.06 \pm 0.06^\circ \text{C.}$  $m = 0.630$ 

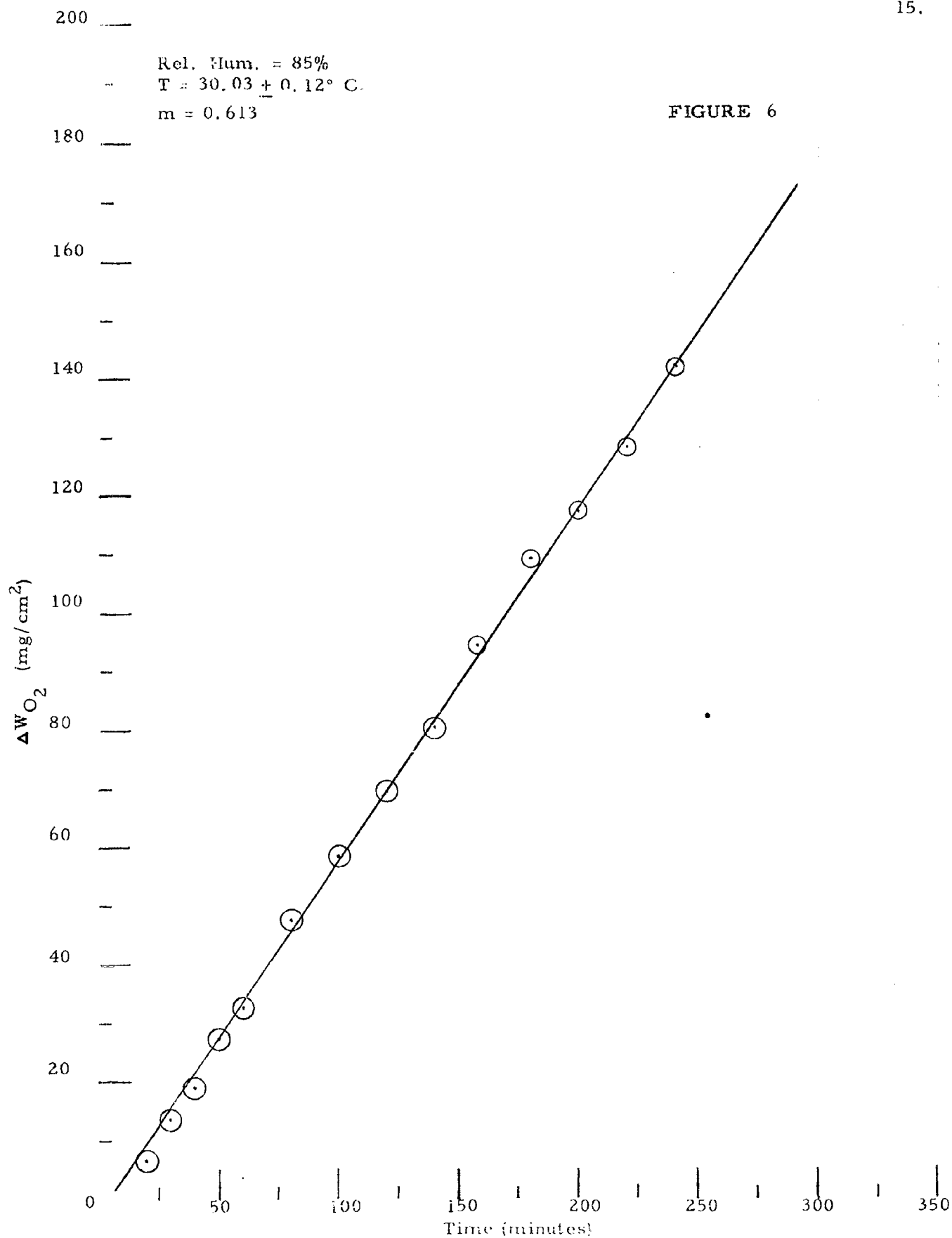
FIGURE 2

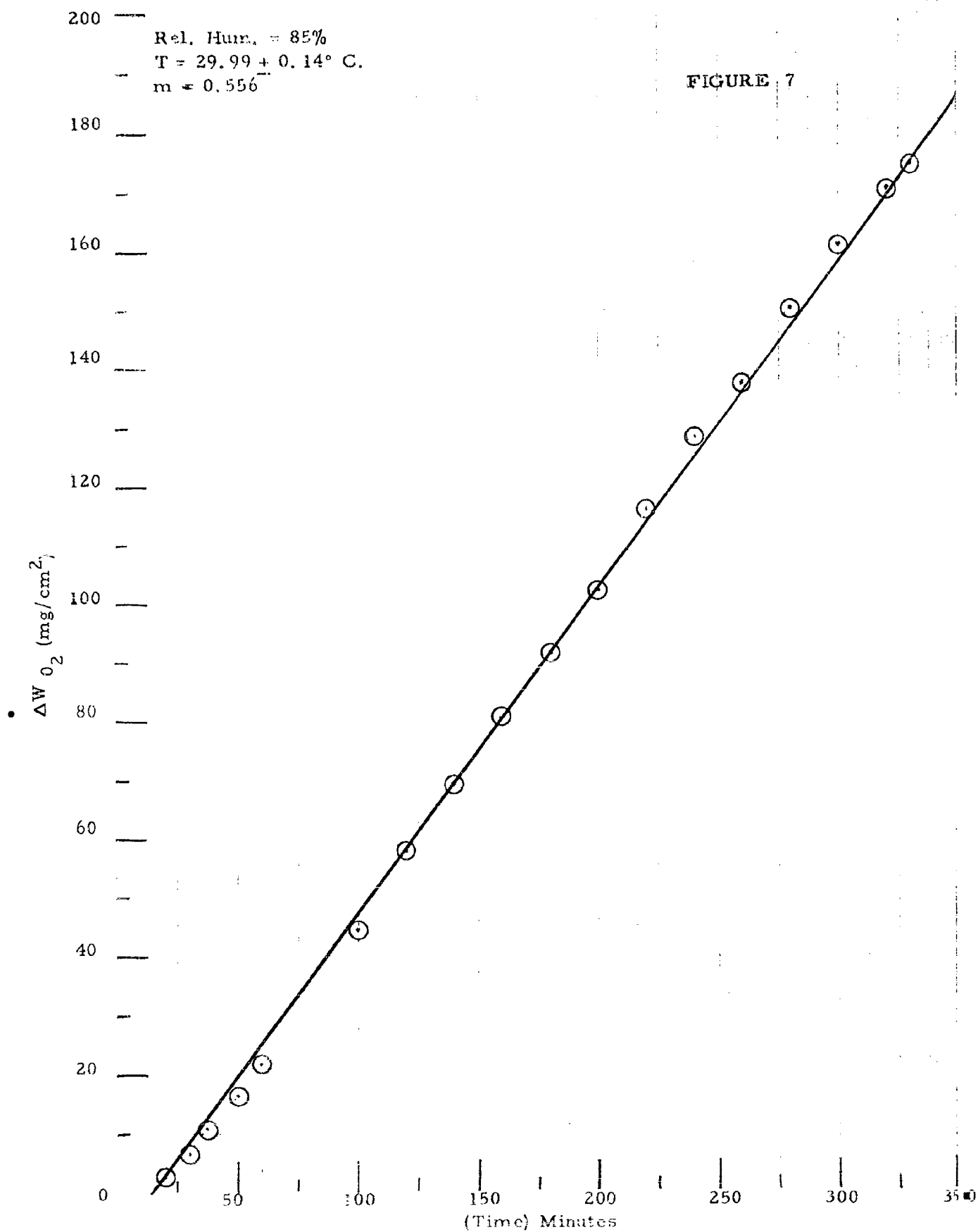


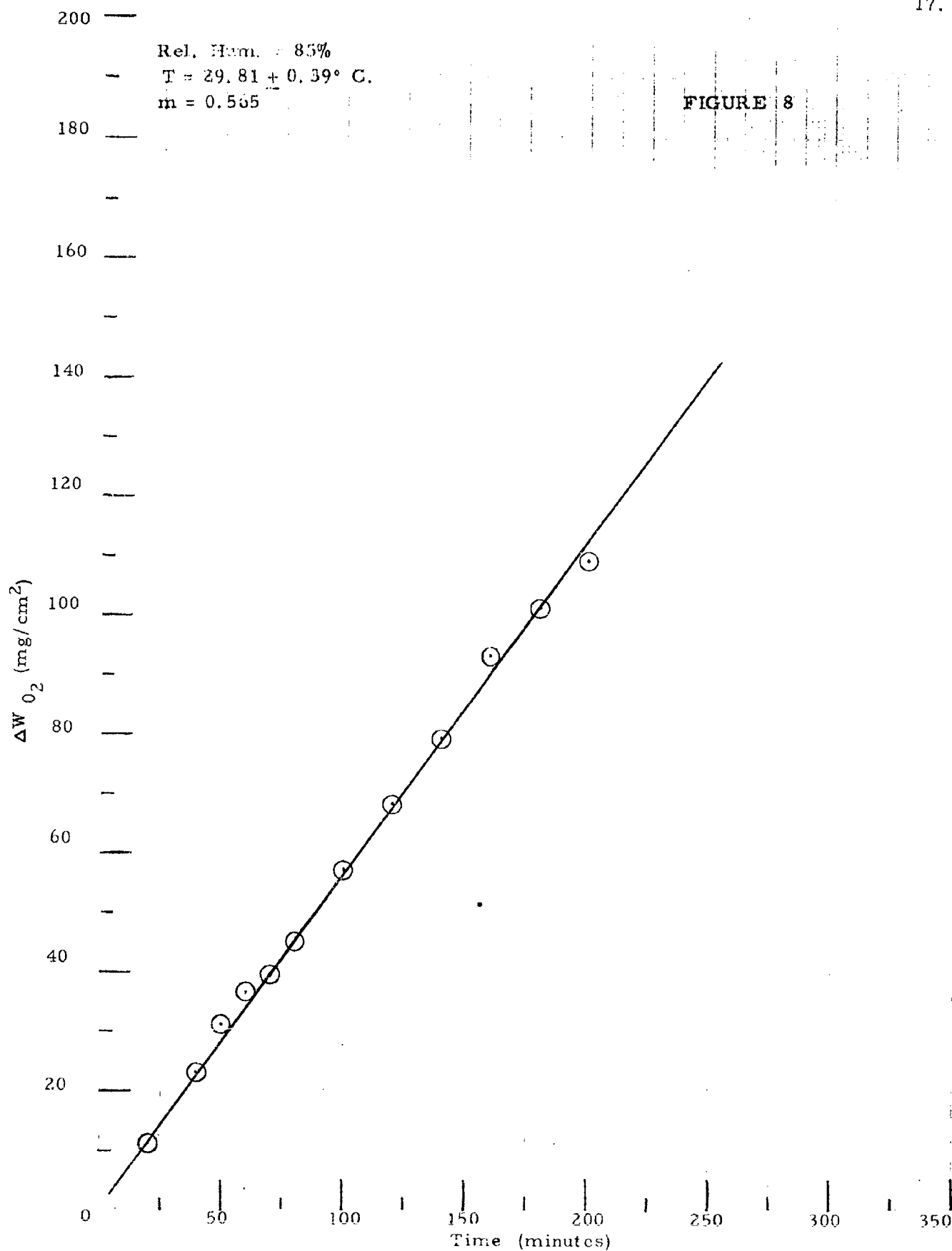


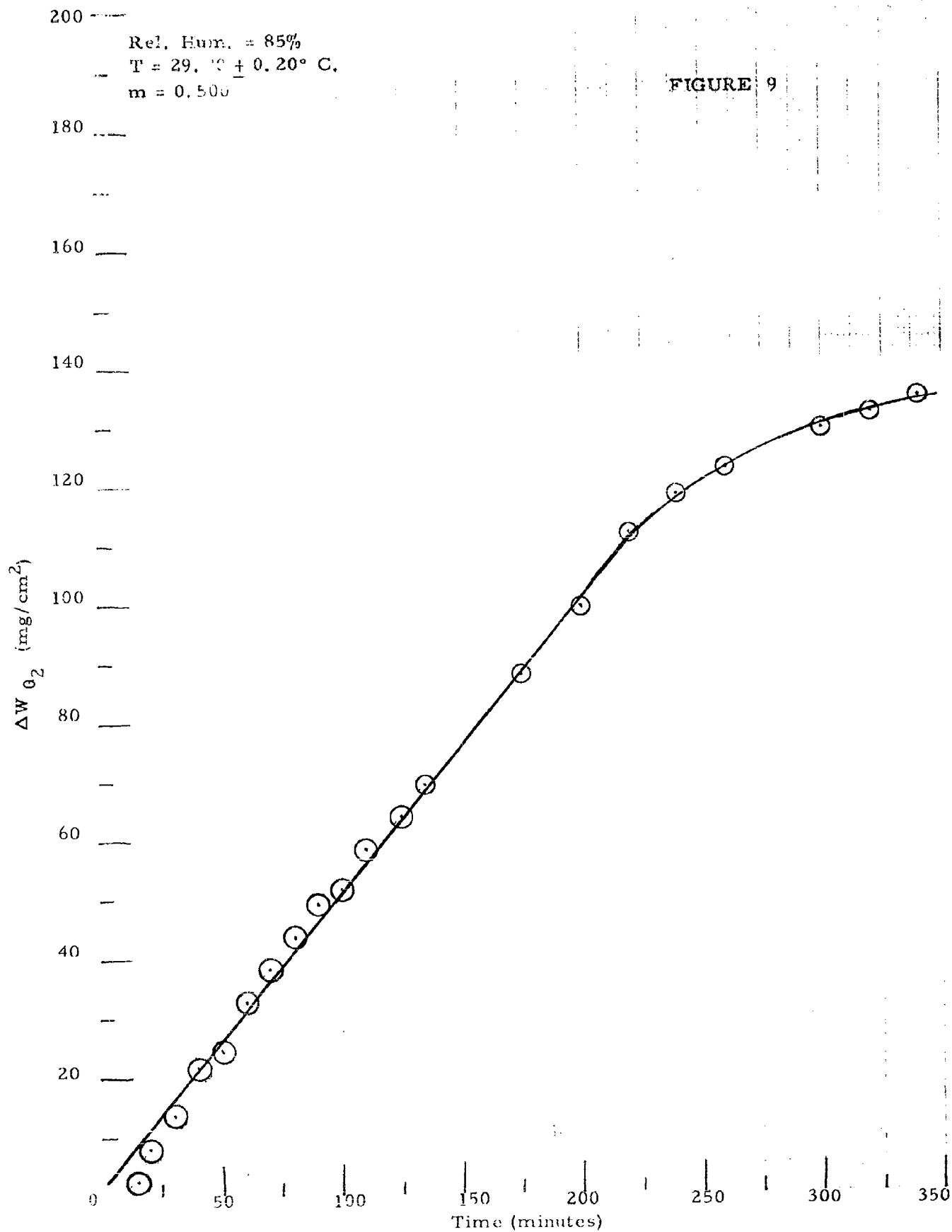


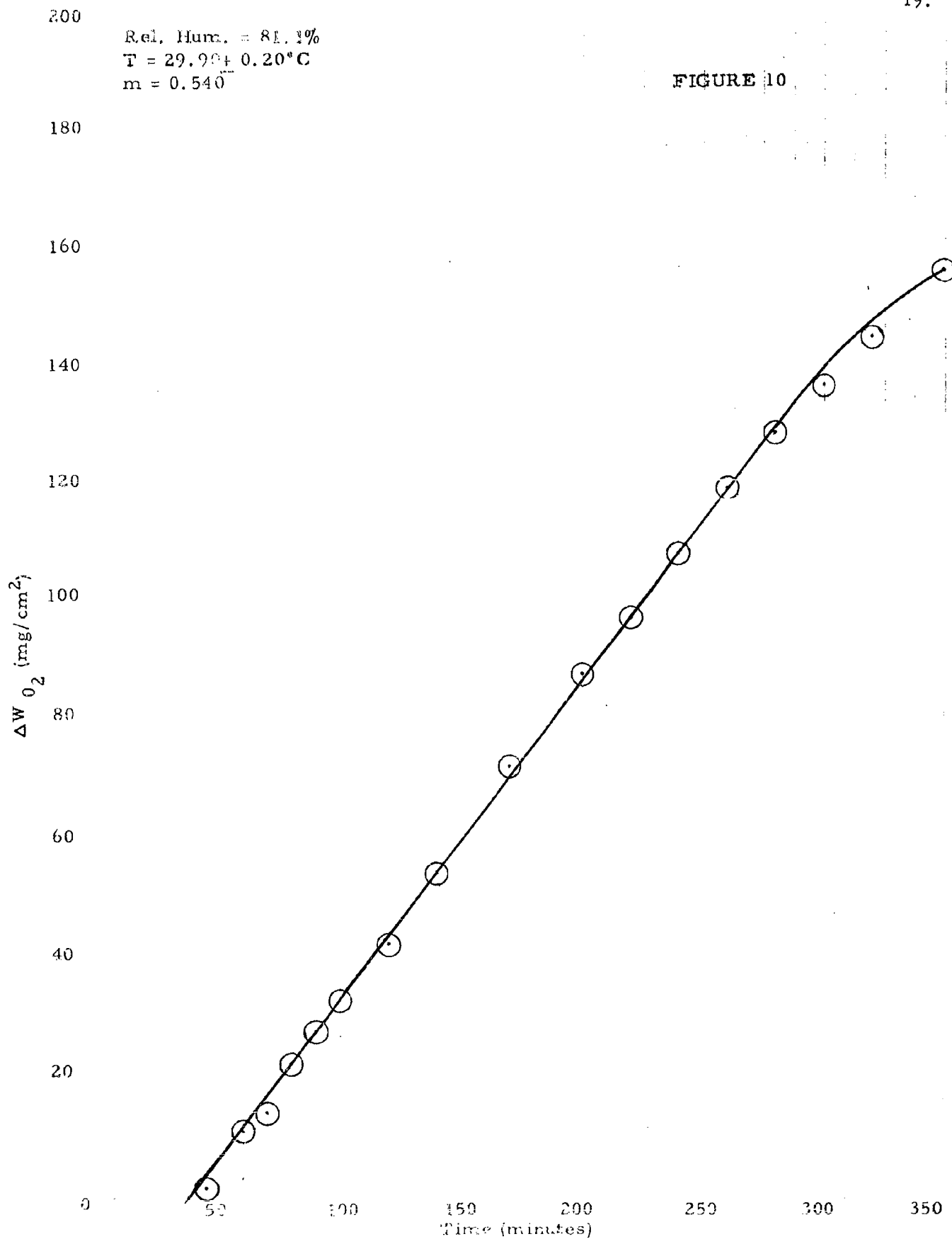






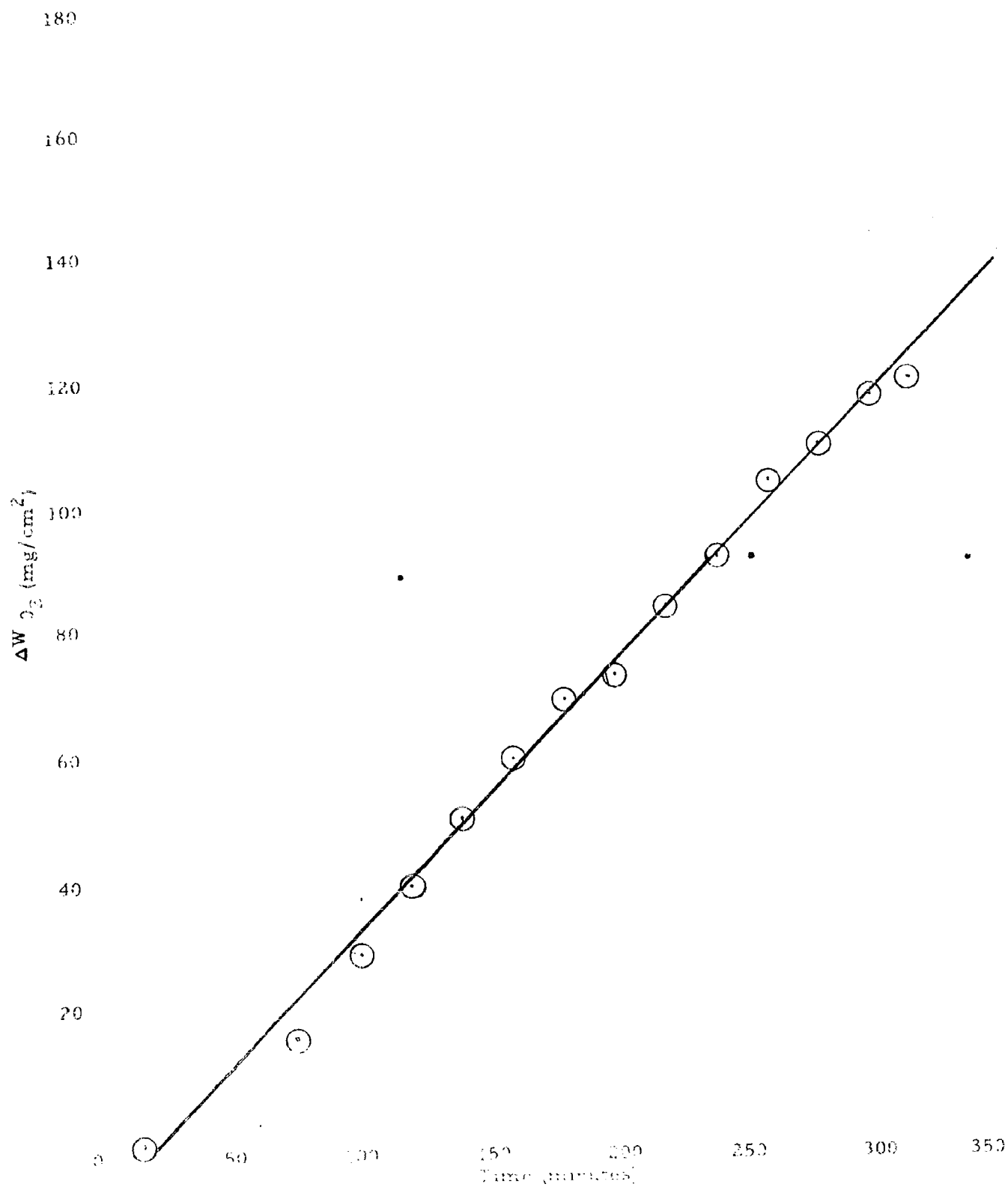


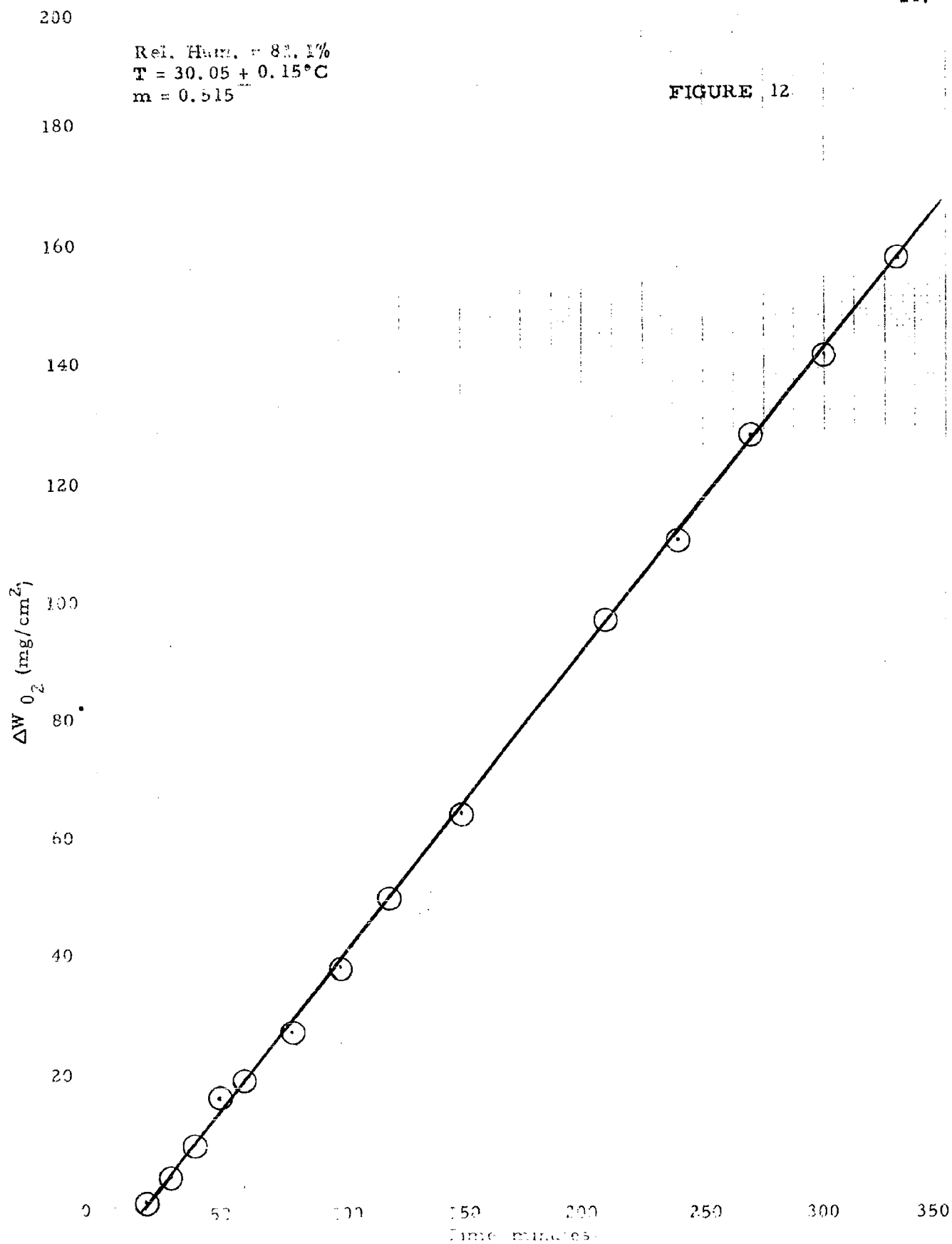


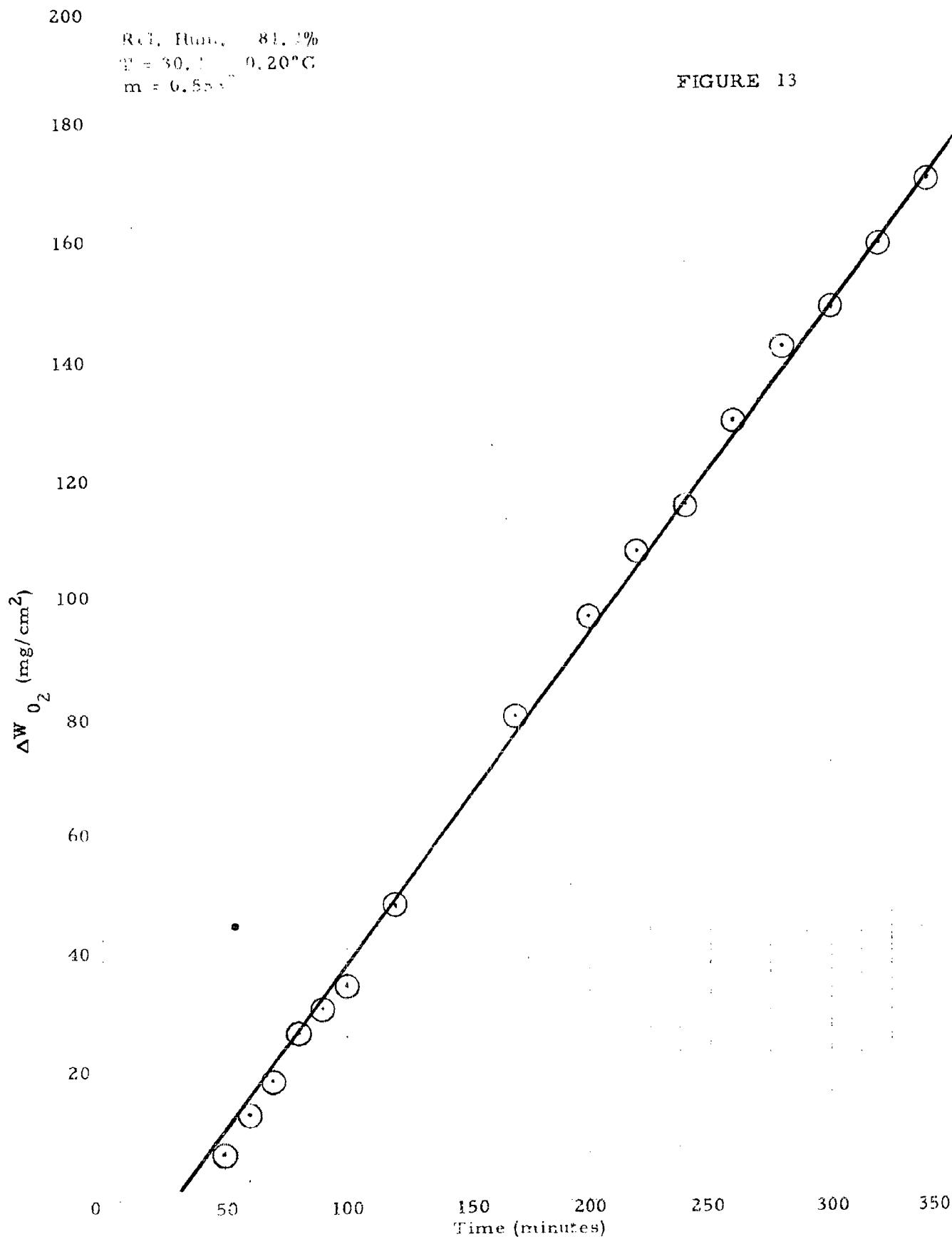


$\text{conc. H}_2\text{O}_2 = 8.1 \text{ g\%}$   
 $T = 30.0 \pm 0.14^\circ\text{C}$   
 $m = 0.43$

FIGURE 11

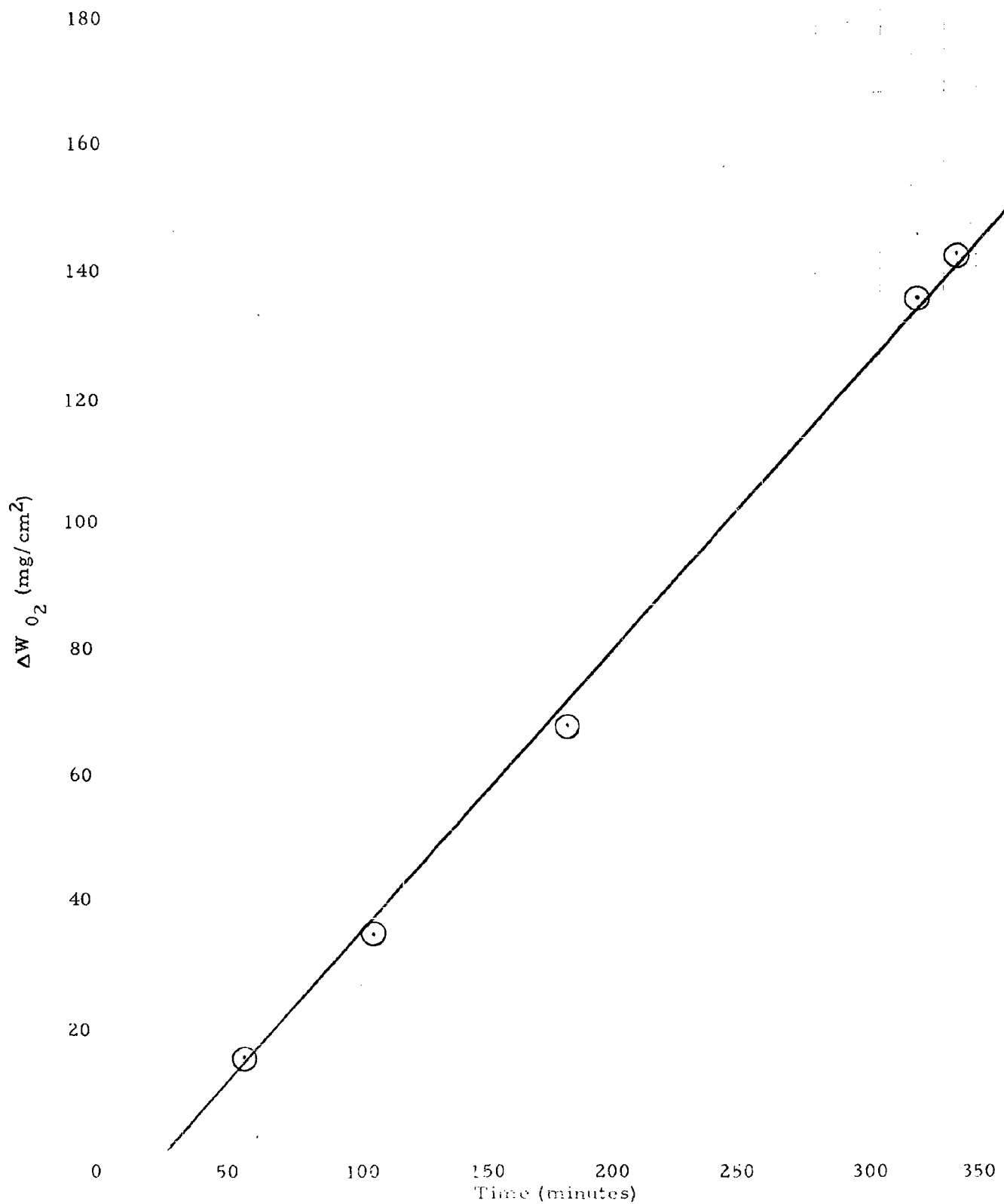






Rel. Hum. = 68.6%  
 $T = 30.21 \pm 0.41^\circ\text{C}$   
 $m = 0.462$

FIGURE 14



200

Rel. Hum. = 68.6%

 $T = 30.1 \pm 0.08^\circ\text{C}$  $m = 0.450$ 

FIGURE 15

180

160

140

120

100

80

60

40

20

 $\Delta W_{O_2} \text{ (mg/cm}^2\text{)}$ 

0

50

100

150

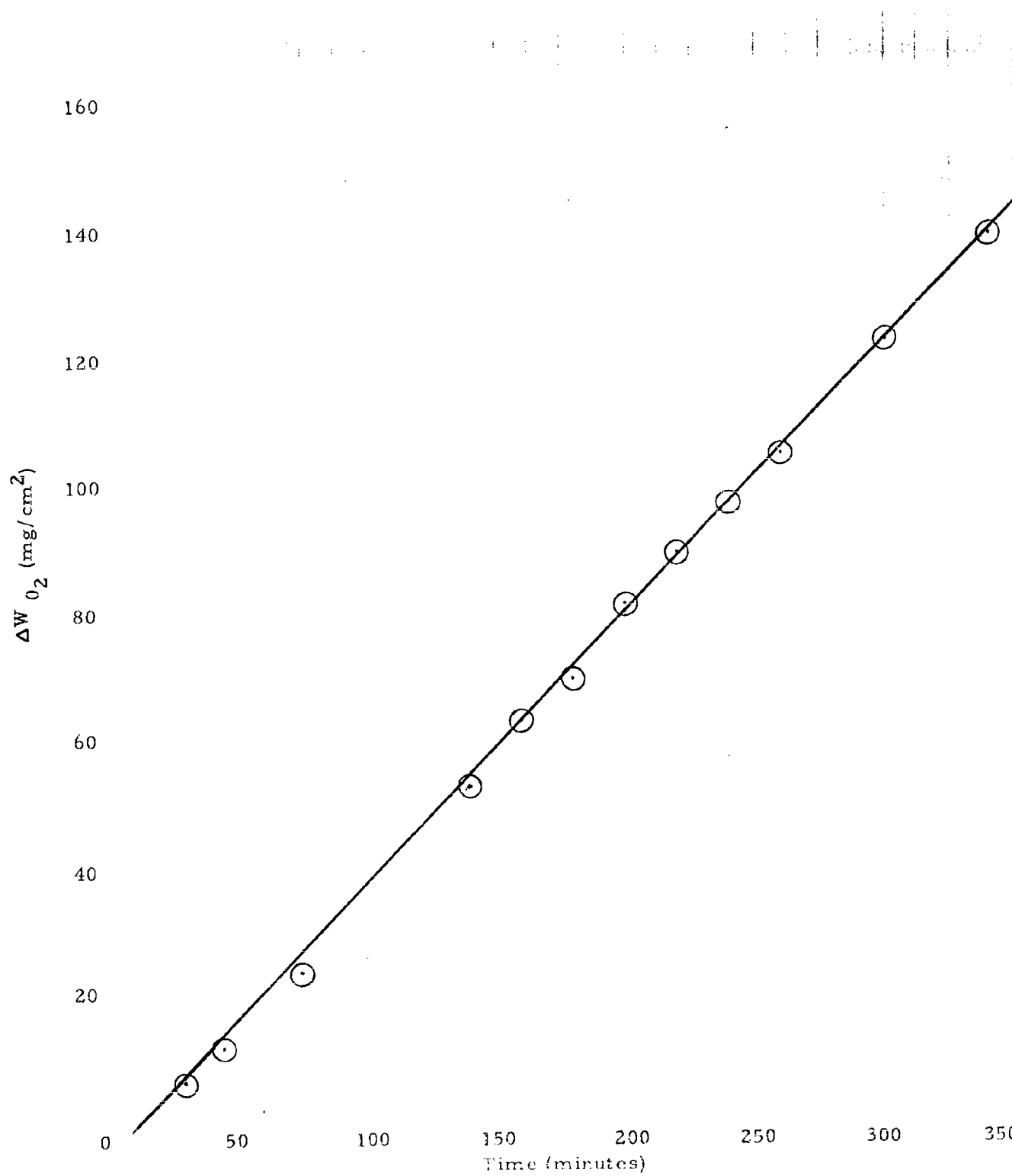
200

250

300

350

Time (minutes)



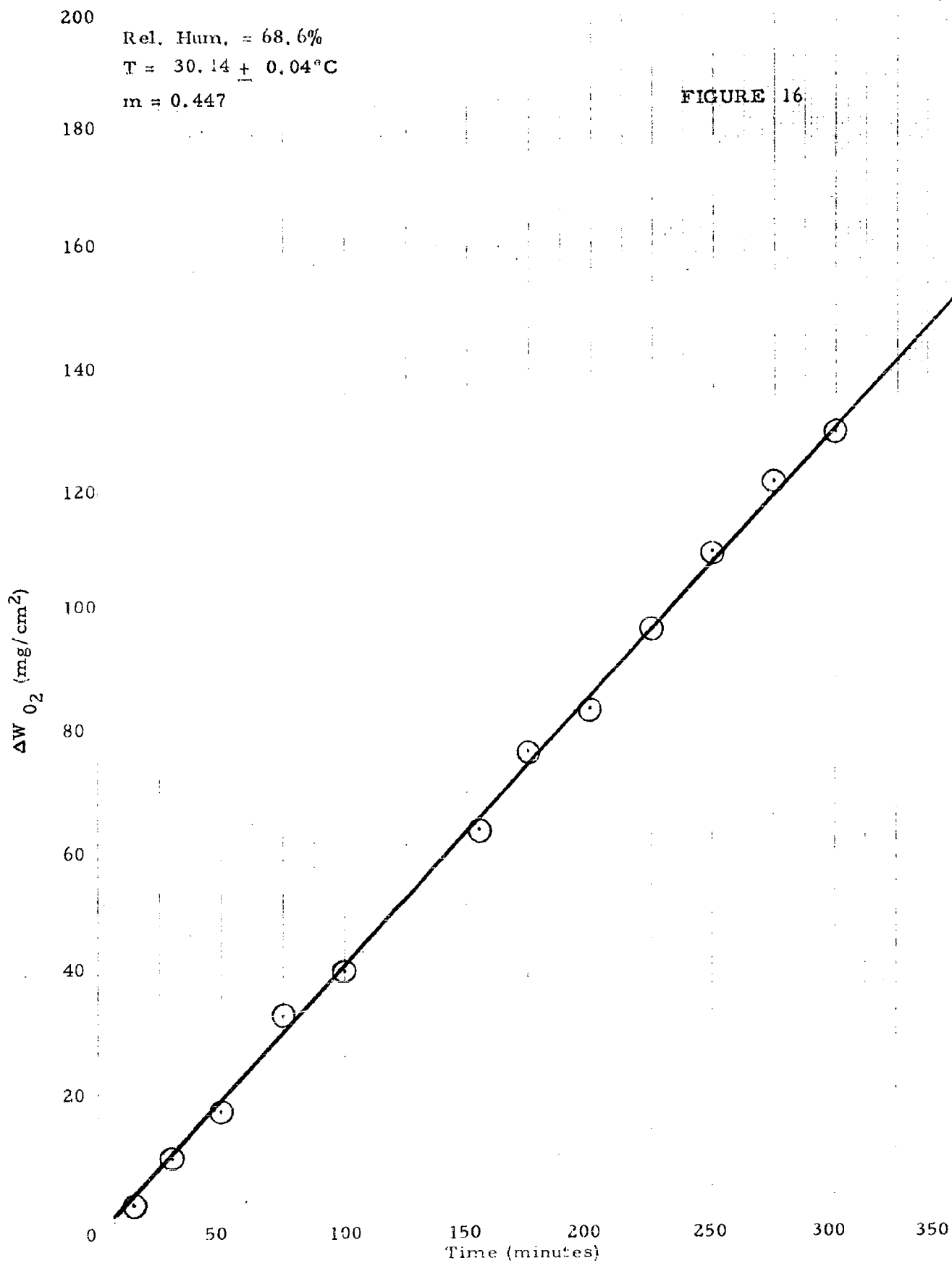
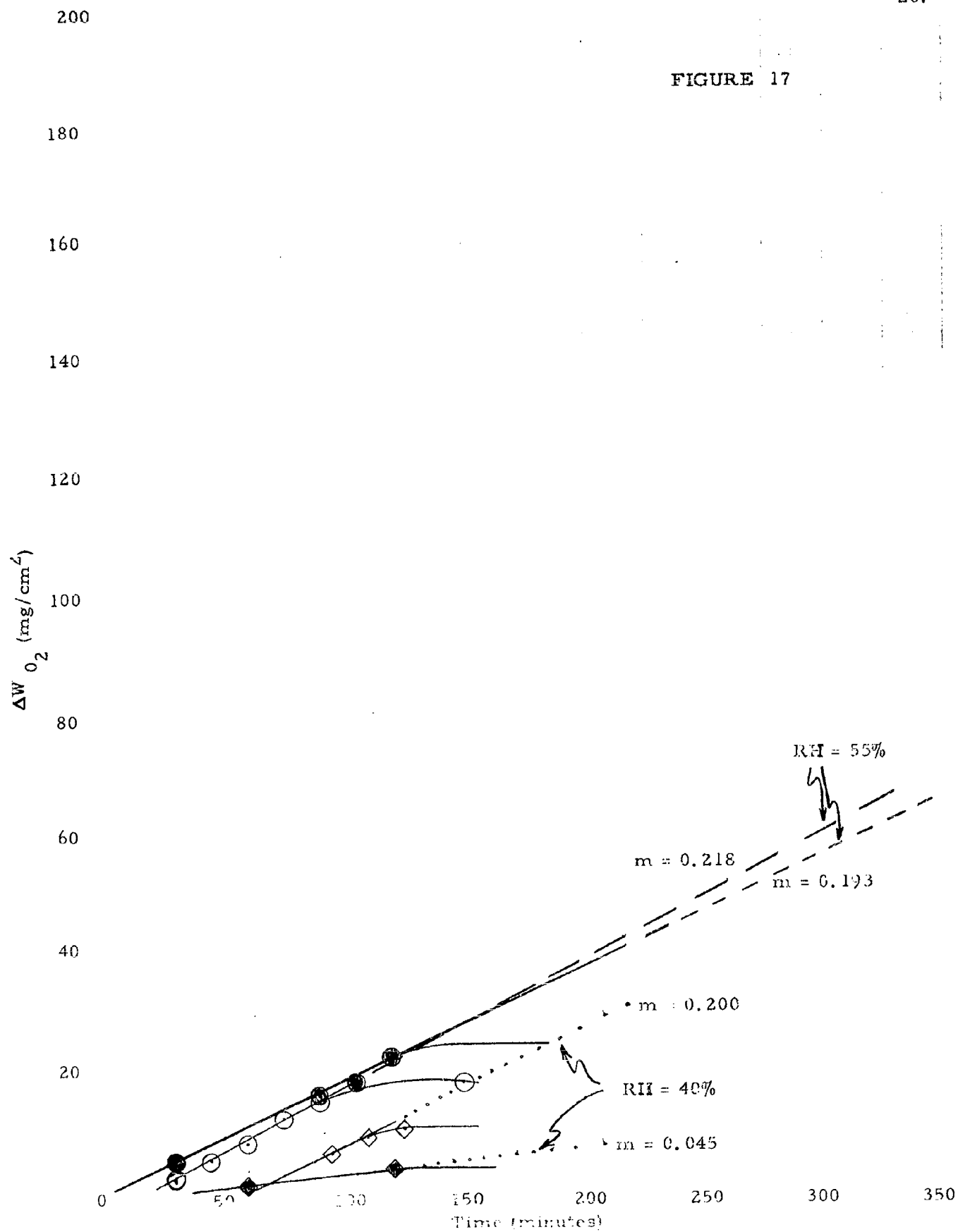


FIGURE 17



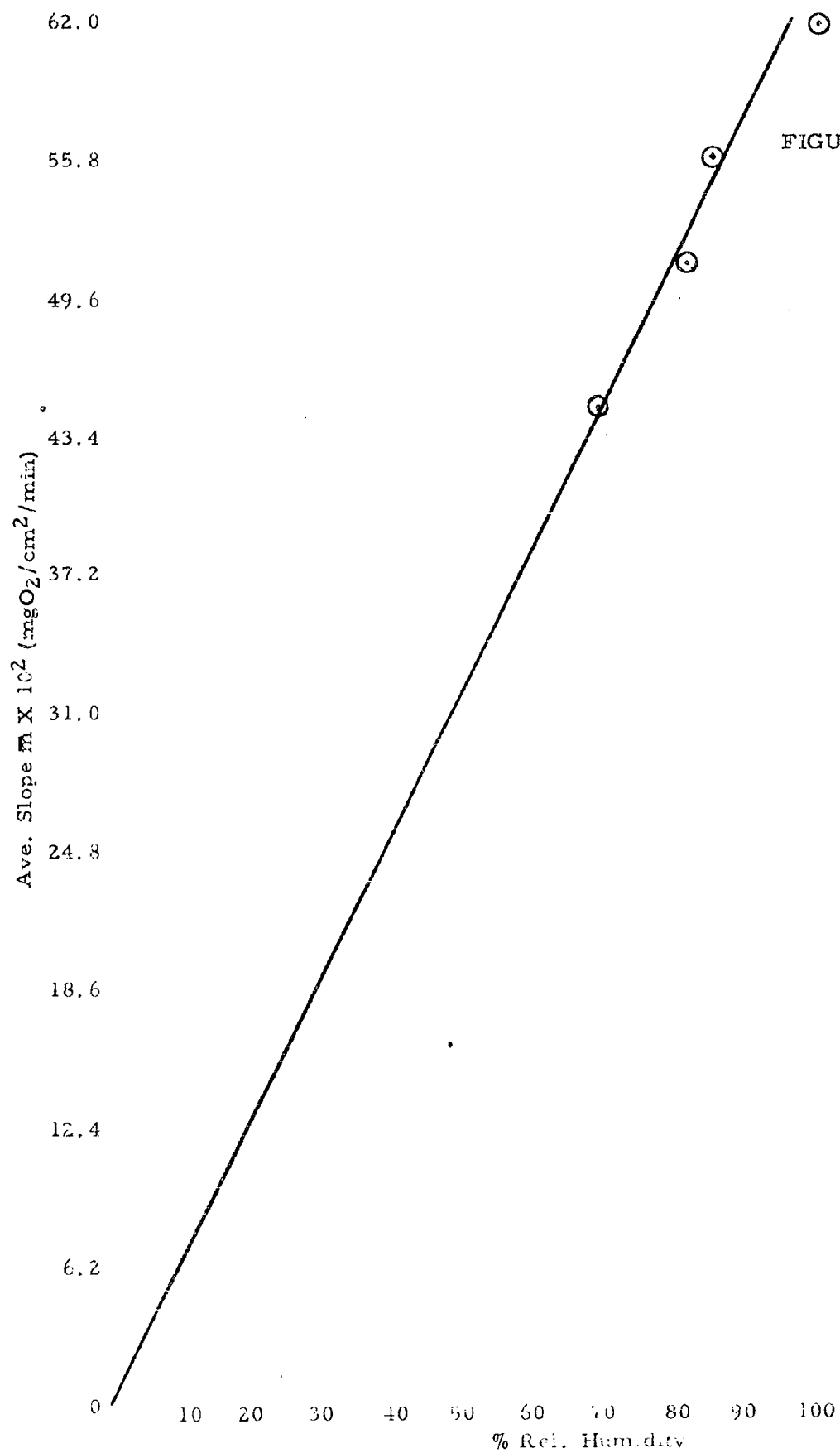


FIGURE 18

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1. Accelerated corrosion of metals

2. Contract DAL18-108-405-CML-518

Seventh Quarterly Report, 14 July 61, 28 pp-18 illus - 2 tables  
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Linear rate of oxdn of Al by HgI<sub>2</sub> attack indicated. Necessity for close temp control & importance of moving atmosphere cited. Various constant RH from 40-100% obtained by satd salt solns. Slopes of oxdn rates decreased linearly with decrease in RH in 68.6-100% RH range where extent of oxdn was 90% theor; in 40-55% RH, 10% theor. Max oxdn rate 0.675 mgO<sub>2</sub>/cm<sup>2</sup>/min @ 100% RH. A time-lapse movie of oxdn at 100% RH was made.

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